EVALUATION OF THE ROLE OF NITROGEN AND PHOSPHOROUS IN CAUSING OR CONTRIBUTING TO HYPOXIA IN THE NORTHERN GULF

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ABSTRACT

Scientific investigations in the Gulf of Mexico have documented a large area of the Louisiana-Texas continental shelf with seasonally-depleted oxygen levels (hypoxia). Nutrient over-enrichment from the Mississippi and Atchafalaya River Basins and stratification in coastal waters are believed to be the major factors contributing to over-production of phytoplankton in the Gulf and the resulting hypoxia. In January 2001, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force adopted the Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico (Action Plan) to address this phenomenon. The Action Plan emphasized reducing nitrogen discharges to the Gulf. During the Environmental Protection Agency (EPA) Region 4 effort to engage in activities under the Action Plan, we took the opportunity to review some of the supporting documents, and some more recently available information. Based upon our review of these materials, we believe the available Gulf hypoxia data and related scientific literature support a modification of the original hypothesis that, for waters subjected to nitrogen and phosphorus loads significantly above historic background levels, there may be considerable benefit to reducing both nutrients in order to restore water quality. While the Action Plan calls for appropriate voluntary action to address nitrogen loading, we present this paper for consideration as part of the 2005 Reassessment of the Hypoxia Action Plan to consider the merits of reducing phosphorus loads as well. A balanced approach to reducing both nutrients also would support achieving the second goal of the Action Plan - to restore water quality throughout the Mississippi River Basin.

This recommendation paper presents the following analysis for peer review: 1) using a more traditional Redfield ratio calculation, the Mississippi River system appears to be phosphorus limited; 2) the observed trend in phosphorus loading data in the River system appears consistent with the two fold increase since 1960 in reactive phosphorus in the Northern Gulf (Rabalais et.al.1999); and 3) the eastern portion of the hypoxic zone also appears to be phosphorus limited and produces the highest concentration of algal production reported in the 1999 Hypoxia Assessment Report.

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INTRODUCTION

Investigations in the northern Gulf of Mexico have documented a large area of the Louisiana-Texas continental shelf with seasonally-depleted oxygen levels (hypoxia). Nutrient over-enrichment from the Mississippi and Atchafalaya River Basins (MARB) is thought to be a primary factor contributing to over-production of phytoplankton and the resulting hypoxia in the northern Gulf. In January 2001, the Mississippi River/Gulf of Mexico Watershed Nutrient Task Force adopted the *Action Plan for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico (Action Plan)* to address this phenomenon. The Action Plan emphasized reducing nitrogen discharges to the Gulf. The management action recommendation was based in large part upon the following premises: 1) the MARB nutrient ratio for nitrogen and phosphorus was in Redfield balance; 2) there has been more than a three-fold increase in nitrogen concentrations in the MARB and northern Gulf since 1960; 3) trends in MARB phosphorus loads cannot be statistically evaluated due to limited historical data; 4) the western portion of the hypoxic zone is predominately nitrogen-limited, especially in late summer (Rabalais et al., 1999); and 5) water quality model predictions indicated that bottom water dissolved oxygen concentrations in the Gulf hypoxia zone would increase in response to nitrogen reductions (Brezonik et al. 1999).

There are many uncertainties in our understanding of the long-term changes in water quality in the MARB and northern Gulf ecosystem. Sensitivity analysis of water quality model parameters showed high uncertainties in the response of dissolved oxygen and chlorophyll concentration in the northern Gulf under different nitrogen reduction scenarios (Brezonik, et al., 1999). Furthermore, water quality model results were not significantly different in predicted responses to reductions in nitrogen and phosphorus (Brezonik et al., 1999). Long-term changes in land cover/land use throughout the MARB have altered water quality and quantity in the basin, and these changes are reflected in a number of eutrophication-related symptoms (Turner and Rabalais, 1991; Justic et al., 1993, 1995). Previous estimates of the nutrient composition of the lower MARB (Turner and Rabalais, 1991; Justic et al., 1995a, 1995b; Rabalais et al., 1999), calculated as the ratio of dissolved nitrate (or dissolved inorganic nitrogen, DIN) to total phosphorus (TP), indicated that the lower MARB had attained stoichiometric balance based on the concepts of Redfield (Redfield, 1934, 1958; Falkowski, 2000). However, the dissolved inorganic phosphorus (DIP) or orthophosphate pool is typically one-third to one-tenth of the TP pool in the MARB (Goolsby et al., 1999) and is the only form directly utilized by autotrophs. Following the concepts of Redfield, the more traditional and perhaps informative comparison of the nutrient composition in the lower MARB would be the DIN: DIP ratio. In this report, we re-assessed the question of nutrient balance in the lower MARB by evaluating existing data on nutrient concentrations

from gauge stations, and discuss the implications for future nutrient control strategies needed to address Action Plan goals.

APPROACH

Water quality data were analyzed from four key monitoring stations (Figure 1):

- (1) The USGS Belle Chasse water quality station #07374525 is located at River Mile 76, approximately 10 miles below New Orleans. The USGS Belle Chasse water quality station is located below all the major cities on the river and below all the major point source discharges. There are useful water quality nutrient records at Belle Chasse starting in 1981. Unfortunately, this station was partially terminated in the early 1990s and water quality records subsequent to that time are sporadic. Due to the paucity of other reliable water quality data from below New Orleans in recent years, the recent USGS Belle Chasse data included in (WEB site was the analyses. http://water.usgs.gov/nwc/NWC/water_quality/tables/sum.07374525.nut.a.html)
- (2) The USGS Tarbert Landing water flow monitoring station #07373291 located at river mile 306 just below the Old River Outlet. There are no major streams entering the Mississippi River below this station and the recorded flows are a reasonable approximation of the flows in the Lower Mississippi River from St. Francisville to Head of Passes. (WEB Site http://nwis.waterdata.usgs.gov/nwis/discharge/?site no=07373291&agency cd=USGS)
- (3) The USGS station at Morgan City, LA #07381600 provided water quality data for the lower Atchafalaya River at a point near where the river discharges into the coastal waters of Atchafalaya Bay before entering the Gulf, approximately 80 miles southwest of New Orleans. (WEB Site http://water.usgs.gov/nwc/NWC/water_quality/tables/sum.07381600.nut.a.html)
- (4) The Army Corps of Engineers (ACOE) water flow monitoring station at Simmesport, LA provided flow records for the Atchafalaya River.

Waters flowing past the Belle Chasse and Morgan City stations transport suspended and dissolved constituents from the entire MARB. Concentrations of DIN (nitrate + nitrite + ammonium) and DIP (orthophosphate) and the DIN: DIP ratios were determined at each river gauge station. Nutrient loadings were calculated using FLUX (Walker 1999). FLUX is an interactive program designed for use in estimating the loadings of nutrients or other water quality components passing a tributary sampling station over a given period of time. The loading estimates are typically used in formulating

reservoir nutrient balances over annual or seasonal periods appropriate for application of empirical eutrophication models. Data requirements include (a) grab-sample nutrient concentrations, typically measured at a weekly to monthly frequency for a period of at least 1 year, (b) corresponding flow measurements (instantaneous or daily mean values), and (c) a complete flow record (mean daily flows) for the period of interest. Using six calculation techniques, FLUX maps the flow/concentration relationship developed from the sample record onto the entire flow record to calculate total mass discharge and associated error statistics. An option to stratify the data into groups based upon flow, date, and/or season is also included. In many cases, stratifying the data increases the accuracy and precision of loading estimates. Uncertainty is characterized by error variances of the loading estimates. Complete description of FLUX in BATHTUB User Manual can be obtained at the following WEB site. (WEB Site

http://www.wes.army.mil/el/elmodels/index.html#wqmodels) (Walker, 1999).

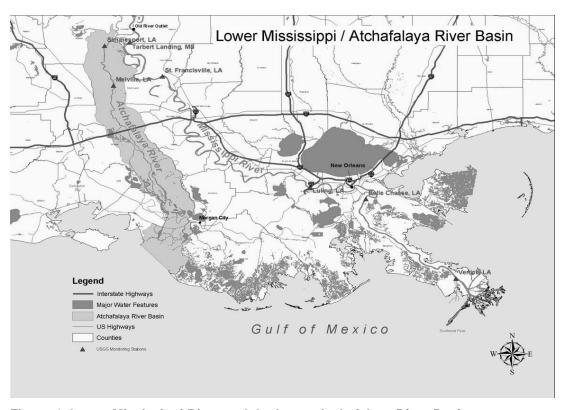


Figure 1. Lower Mississippi River and the Lower Atchafalaya River Basin

The DIN: DIP elemental ratios presented below were calculated using dissolved N and P measurement parameters:

- Ammonia, water, filtered, milligrams per liter as nitrogen (NH₄-N)
- Nitrite plus nitrate, water, filtered, milligrams per liter as nitrogen ((NO₂+NO₃)-N)
- Orthophosphate, water, filtered, milligrams per liter as phosphorus (PO₄-P)

The DIN: DIP elemental ratio was obtained using the formula:

$$DIN:DIP = \frac{\frac{NH_4 - N(mg/L) + (NO_2 + NO_3) - N(mg/L)}{14}}{\frac{PO_4 - P(mg/L)}{31}}$$

The DIN was obtained as the sum of concentrations (in mg/L) of dissolved NH_4 -N and dissolved NH_4 -N. The DIP is equal to the concentration of dissolved PO_4 -P. The equation constants 14 and 31 represent the atomic weights of N and P, respectively. The DIN: DIP elemental ratio was obtained for each simultaneously observed set of parameters listed above. This elemental ratio was calculated as dissolved NH_4 -N plus dissolved NO_2 +NO₃-N divided by dissolved PO_4 -P multiplied by the constant 31/14.

RESULTS

The annual average FLUX-calculated mass transport loads for DIN and DIP at Belle Chasse were 2,017 and 114 metric tons per day (mt/d), respectively. The annual average concentrations of DIN, and DIP at Belle Chasse during the period 1980 to 1999 were 1.4 mg/L DIN, 0.09 mg/L DIP, which is equivalent to 102 μ M DIN and 2.9 μ M DIP. For comparison the annual mean TP concentration was 0.21 mg/l (Table 1). In Figures 2 and 3, the time series plots of DIN and DIP are plotted for the Belle Chase sampling station. These plots illustrate the seasonal and climatic variability in nutrient concentrations in the River system.

The annual average FLUX-calculated mass transport loads for DIN and DIP at Morgan City were 612 mt/d and 28 mt/d, respectively. The annual average concentration of DIN and DIP during the period 1980 to 1999 was approximately 0.96 mg/L or 70 μ M DIN and 0.05 mg/L or 1.8 μ M DIP. The annual average TP concentration was 0.22 mg/l (Table 2). In figures 4 and 5, the time series plots of DIN and DIP indicate significant seasonal and climatic variability. In addition, there appears to be no apparent net increase or decrease in nutrient concentrations since the mid 1980s.

Table 1. Mean Chemical Concentrations at Belle Chasse

USGS Monitoring Station 1980 - 1999

Nutrient	Units	Mean	Standard Deviation	25 th Percentile	75 th Percentile
DIN	mg/L	1.4	0.53	1.1	1.7
DIP	mg/L	0.09	0.06	0.06	0.11
TP	mg/L	0.21	0.087	0.14	0.27

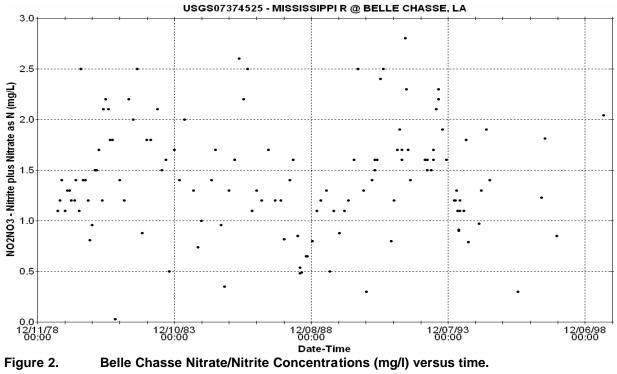


Figure 2.

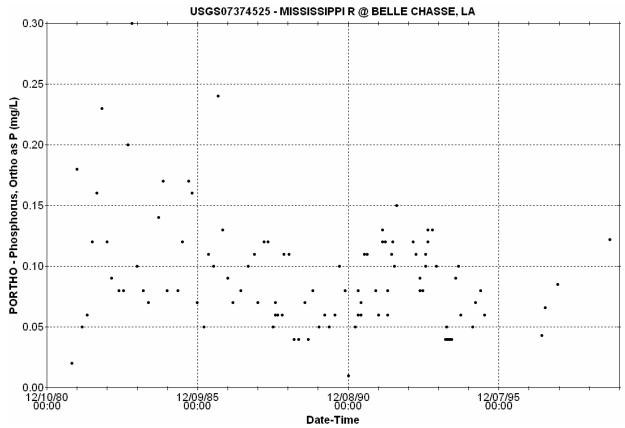


Figure 3. Belle Chasse Othro-Phosphorous Concentration (mg/l) versus time.

Table 2. Mean Chemical Concentrations at Morgan City

USGS Monitoring Station 1980 - 1999

Nutrient	Units	Mean	Standard Deviation	25 th Percentile	75 th Percentile
DIN	mg/L	0.96	0.46	0.7	1.2
DIP	mg/L	0.05	0.02	0.04	0.06
TP	mg/L	0.22	0.29	0.11	0.25

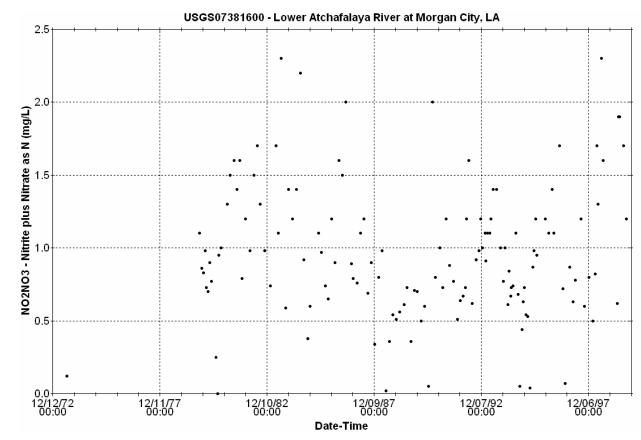


Figure 4. Morgan City Nitrate/Nitrite Concentrations(mg/l) versus time.

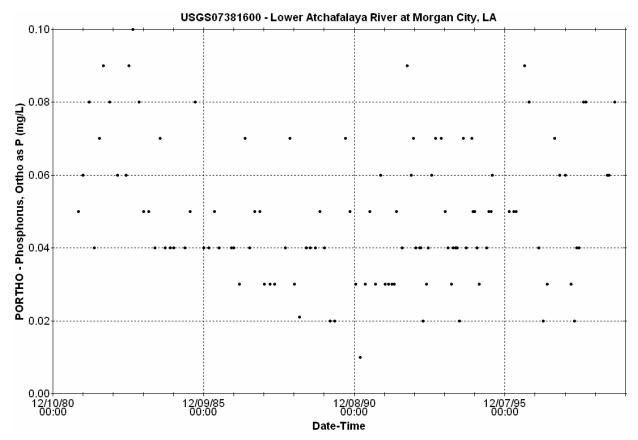


Figure 5. Morgan City Ortho-Phosphorous Concentration (mg/l) versus time.

Mean monthly DIN: DIP ratios, calculated at Belle Chasse and Morgan City during the period 1980 to 1999, were higher during the late winter to spring (February to June) when the river flows are high than during summer low flow periods (Figure 6). DIN: DIP ratios during the spring deviate from Redfield proportions (16:1) by a factor of approximately 3 (Table 3). Lohrenz et al. (1999) also reported high nutrient ratios in the lower Mississippi River and found that the high ratios were strongly correlated with high flows. A comparison of monthly elemental ratios for the Belle Chasse station calculated using DIN: DIP and DIN: TP indicate that the elemental ratios calculated using DIP are much larger and seasonally variable (Figure 7).

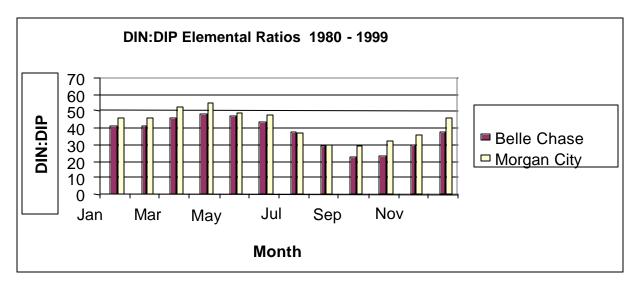


Figure 6. Average Monthly DIN/DIP ratios for Belle Chasse and Morgan City 1980 to 1999

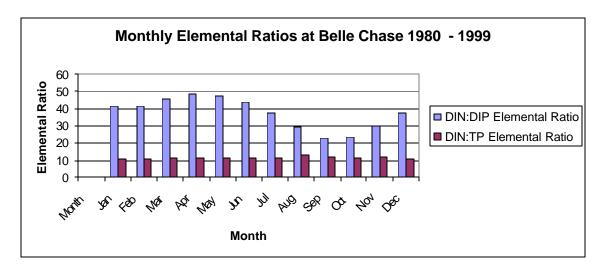


Figure 7. Monthly Elemental Ratios (DIN: DIP and DIN: TP) at Belle Chasse

Table 3. Annual Average and Spring Time DIN: DIP Elemental Ratios

	Belle Chasse	Morgan City	Average
Annual Average DIN: DIP Elemental Ratio	37	42	39.5
Spring Time (February - June) Average DIN: DIP Elemental Ratio	47	52	49.5

DISCUSSION

The lower Mississippi/Atchafalaya River Basin (MARB) discharges an average of 952,700 metric tons of nitrogen as nitrate each year (Goolsby, et al., 1999). Nitrate concentrations and mass flow are generally highest during the late winter/spring periods. The MARB discharges an average of 41,770 metric tons annually of phosphorus as orthophosphate (Goolsby et al. 1999).

For more than 50 years, oceanographers and marine scientists have recognized that the elemental composition of phytoplankton is remarkably similar to that of the seawater in which they are found (Redfield, 1934, 1958, Falkowski, 2000). In his 1958 publication, Albert Redfield established the so-called Redfield elemental ratio (106 C: 16 N: 1 P, by atoms), based on the concentrations of inorganic nitrogen and phosphate. Although Redfield's analysis dealt exclusively with nitrate to phosphate ratios, it has become common (and accepted) in the literature to include all forms of dissolved inorganic nitrogen (nitrate, nitrite, and ammonium); thus, DIN to DIP ratios are now most commonly used to evaluate elemental ratios in seawater. We have chosen the latter procedure for calculating elemental ratios. Significant deviations from the Redfield ratio provide information on the potential for one nutrient to be used up by phytoplankton while leaving "surpluses" of the other nutrient. Elemental ratio information often is useful for contributing to decisions regarding nutrient management strategies to control the excess growth of phytoplankton. Elemental ratios must be calculated properly and the results must be correctly interpreted in order to provide useful information for decision-making. Elemental ratios are only one parameter essential for making decisions regarding nutrient reduction.

Comparison of the River System Redfield Ratios Using Total phosphorus (TP) and DIP

The Redfield ratios for the River System in this paper have been calculated using the traditional DIN and DIP components. The Redfield ratios, especially in spring and early summer are well above the 16:1 ratio associated with a balanced nutrient condition. The analysis in the CENR report (Table 4) based the River System nutrient ratio on DIN and TP. The ratios using TP are 14-15:1 and they are used to assert the River is in nutrient balance as compared to the Redfield ratio traditionally calculated using DIP. Interestingly, the nutrient ratio for the Northern Gulf in Table 4 is calculated using reactive phosphorus or DIP and has a value of 24:1. The mean DIN: DIP elemental ratios for the Mississippi River system have an annual average of 39.5 and a spring season average of 49.5, indicating a nutrient imbalance (Table 3). This difference in calculating the nitrogen and phosphorus nutrient ratios has a profound impact on the interpretation of the data.

During the spring and early summer in waters in the Northern Gulf influenced by the Mississippi River, ratios of ambient concentrations of DIN: DIP have often been found to be much higher than the Redfield ratio (Lohrenz et al. 1999, Ammerman, 1992, Chen, 2000, Smith and Hitchcock, 1994, Dortch et al. 1992, Nelson 2003, (personal communication), and Dortch 2003 (personal communication).

Assessing the Relative Increase in Nitrogen and Phosphorus Loads in the River System Both nitrogen and phosphorus concentrations have increased significantly in the Northern Gulf of Mexico from 1960 to 1987 (Table 4 Rabalais (1996) and Justic(1995)). This observation indicates that the Northern Gulf of Mexico is over-enriched with respect to both nitrogen and phosphorus. The

predominant source of these nutrients is the Mississippi River System.

The CENR Report documented the DIN in the River System increased by a factor of 3.3 from 1960 to 1987 as summarized in Table 4. However, the report concluded that there was insufficient phosphorus data to statistically calculate the relative change in load with respect to time. A plot of the historic nitrogen and fertilizer use in the United States is presented in Figure 8, from (Rabalais et. al., 1999), and the data clearly indicates that both nitrogen and phosphorus fertilizer use have increased significantly from the 1920s. Interestingly, if one compares the relative increase in phosphorous and nitrogen fertilizer use from 1960 to the 1981-1987 time period in Figure 8 with the 1960 and the 1981-1987 calculated concentration values for the Northern Gulf in Table 4, there appears to be comparable relative increases for both nutrients. Given that the nitrogen increase is statistically verified we also infer that the calculated phosphorus concentration increase in the Northern Gulf since 1960 is likely due to an increase in phosphorus loads from fertilizer use and municipal and industrial discharges due to population growth impacts in the Mississippi River Basin. We cannot identify another likely source of excess phosphorus in the Northern Gulf.

In addition, EPA's ecoregion-based nutrient criteria development documents published in 1998 recommended TP and total nitrogen (TN) criteria values ranging from 0.01 – 0.076 mg/l TP and 0.12 -2.18 mg/l TN, for the ecoregions in the Mississippi River Basin. (The 2.18 mg/l value is for the western cornbelt and is much higher than the other ecoregion TN values.) These values represent the TN and TP concentrations empirically determined to inherently protect healthy and balanced aquatic communities in the watersheds and mainstem rivers. Each state is currently developing nutrient criteria development plans to adopt these criteria, or other scientifically

defensible criteria, in a "reasonable " timeframe. These nutrient criteria, even if additional data support somewhat less stringent values, could not be achieved without significant TN and TP load reductions in most sub-watersheds as evidenced by the significantly higher average TP concentration, 0.21 mg/l, and average DIN concentration, 1.4 mg/l, currently present in the lower Mississippi River system.

Table 4. Comparison of nutrient concentration changes in the Mississippi River and Northern Gulf of Mexico. Data from Table 5.1 of the Hypoxia Characterization report (1999).

Nutrient Concentrations and Average A		Mississip	pi River	Northern Gulf of Mexico		
		1960–62⁴	1981–87	1960⁵	1981–87	
Nutrient Conce	entrations (µM)					
Nitrogen ¹	Mean 36.5 No. of Data 72 Standard Error 2.9		114 200 6.0 (p < 0.001)	2.23 219 0.16	8.13 219 0.60	
Phosphorus ²	Mean No. of Data Standard Error	3.9 - -	7.7 234 0.4 (p < 0.001)	0.14 231 0.01	0.34 231 0.02	
Silica ³	Mean No. of Data Standard Error	155.1 72 7.5	108 71 4.3 (p < 0.001)	8.97 235 0.55	5.34 235 0.33	
Average Atom	ic Ratios					
Silica:Nitrogen Nitrogen:Phosphorus Silica:Phosphorus		4.2 9 39.8	0.9 15 14	4.0 16 64	0.7 24 16	

 $^{^{1}}$ N-NO $_{3}$ for the Mississippi River, dissolved inorganic nitrogen (DIN = NO $_{3}$ + NH $_{4}$ + NO $_{2}$) for the northern Gulf

²Total P for the Mississippi River, reactive P for the northern Gulf of Mexico.

³Reactive Si.

⁴Turner and Rabalais 1991 for N and Si, reconstructed for P.

⁵Reconstructed data.

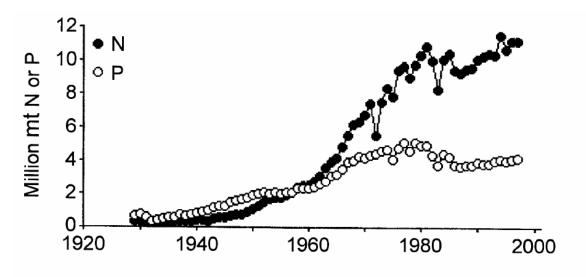


FIGURE 5.12. Nitrogen (as N) and phosphorus (as P₂O₅ equivalent) fertilizer use this century in the United States up to 1996–97. (*Modified from Turner and Rabalais 1991*.)

Figure 8. Trend of Nitrogen and Phosphorus Use in the United States

Hypoxic Zone Evaluation

The following data from the July 1994 LATEX study (Rabalais et. al., 1999 Figures 6.5 –6.7) indicate that the Hypoxic Zone is initially phosphorus limited and the chlorophyll_a concentrations are greatest, an indicator of algae production, in the eastern portion of the Hypoxic Zone, West longitude 89-90. The July 1994 LATEX data in (Rabalais et. al., 1999 Figure 6.5) clearly indicates that there is a pronounced east-west decreasing gradient in surface water algal biomass during this sampling period. This trend positively correlates with the nutrient concentration gradients presented in (Rabalais et. al., 1999 Figure 6.6.) In addition, the ratio of surface-to-bottom algal pigment concentrations indicate that the eastern portion of the hypoxic zone is dominated by active surface algae and the western portion is dominated by decaying bottom algae (Rabalais et. al., 1999 Figure 6.7).

Interestingly, the reactive ortho-phosphate concentrations appear to be relatively constant in the Hypoxic Zone downstream of the initial algal production zone (Rabalais et. al., 1999 Figure 6.6). This phenomenon could be influenced by a variety of factors such as the likely re-mineralization of phosphates from decaying biomass produced earlier in the season when the nutrient loads from the River system is much greater. When the bottom of the water column becomes anoxic, soluble Phosphorous may be rapidly released into the water column, while nitrification/de-nitrification is hindered, trapping Nitrogen in the system. In this sense, the onset of anoxic conditions may create a cascade of Phosphorous release that further stimulates the algal bloom.

From this data set it is not obvious what would happen under various nutrient load reduction scenarios. For example, if phosphate concentrations were reduced, there would likely be a reduction in the initial biomass production. However, it is likely that the excess nitrogen would be transported further downstream and would be available to produce more algae with the apparently recycled phosphates. The amount of reduction of recycled phosphates available for downstream algal production that would result from reducing initial phosphate concentrations and the reduced initial biomass is unknown but could be significant. Further reducing nitrogen alone would not have much of an impact on the initial algal production unless the reduction was sufficient to create a nitrogen-limited condition. However, reducing the nitrogen load would reduce the amount of excess nitrogen compounds transported downstream in the hypoxic zone that would be readily available to produce algal biomass. Such nitrogen reduction would likely reduce the extent of the hypoxic zone.

Unfortunately there is limited data both spatially and temporally for the entire Hypoxic Zone. It would be instructive to assess how the system biomass and nutrient gradients respond to seasonal variations. Most of the data collected seasonally in the Hypoxic Zone is focused in a particular zone and is summarized below.

Scientists have been studying the growth of phytoplankton in the Gulf of Mexico for many years. In the early 1990s, considerable effort was focused on determining what environmental factors in the Gulf regulated phytoplankton growth and primary production. Dortch and Whitledge (1992) conducted studies in summer 1987 and spring 1988 off of Southwest Pass. This area was characterized by sharp gradients in salinity, turbidity, and nutrients as river water from Southwest Pass mixed with Gulf of Mexico water. As the turbidity decreased, the corresponding increased penetration of sunlight into the nutrient-enriched water stimulated high levels of phytoplankton growth and production. At stations further offshore, nutrient concentrations were reduced to very low levels due to the combination of phytoplankton growth and dilution with high salinity Gulf of Mexico water having very low nutrient concentrations. Using two different approaches to assess nutrient limitation, Dortch and Whitledge (1992) found that the ratio of intracellular free amino acids to protein, an index of nitrogen limitation, did not support the view that nitrogen limitation was widespread. They also used an indirect method to infer which nutrients were limiting, based on concentrations and ratios of inorganic nutrients. This latter approach indicated that potential limitation by phosphorus was more likely than nitrogen limitation in areas of low salinity, especially during spring. The potential for nitrogen limitation was more prevalent in higher salinity waters further offshore, especially during the late summer.

The potential importance of phosphorus as a limiting nutrient has been reported by other studies and this was reviewed in (Rabalais et. al., 1999). Lohrenz et al. (1999) used an indirect approach similar to

that of Dortch and Whitledge (1992) to infer which nutrients were limiting in the northern Gulf of Mexico. They also found evidence for potential phosphorus limitation in lower salinity waters, particularly in spring. Lohrenz et al. (1999) recommended phosphorus reduction in the Mississippi River as a potentially effective measure to control the excess phytoplankton production, especially during the spring and early summer. Smith and Hitchcock (1994) conducted nutrient enrichment bioassays in the Gulf of Mexico during March and September 1991 and May 1992. Their findings were consistent with phosphorus limitation during the spring, especially in the lower salinity waters, and nitrogen limitation in the fall. Other evidence for spring phosphorus limitation in Mississippi River plume waters comes from reported high rates of phosphorus turnover during July and August 1990 and September 1991, particularly in low salinity waters (Ammerman, 1992). Ammerman (1992) also found high activities of alkaline phosphatase, an enzyme that is induced in some phytoplankton under low phosphorus conditions.

Data were acquired from NOAA (http://www.aoml.noaa.gov/ocd/necop/) for three years, 1994, 1995, and 1997, which was part of an extensive data set on nutrient concentrations in the Gulf of Mexico spanning many years (Hendee (1994) and Hendee, personal communication, 2003). Dr. Nancy Rabalais, (Louisiana University Marine Consortium), Dr. R. Eugene Turner, (Louisiana State University), and Dr. William W. Wiseman (Louisiana State University) compiled these data through funding provided by NOAA. The data were from Transect C, which starts in the inshore waters (water depth 5.4 meters) off Terrebonne Bay, near Chauvin, Louisiana, West Longitude 90.5, and runs southeastward for approximately 50 miles to an offshore location where the water depth is approximately 45 meters (See WEB site).

The DIN and DIP surface data from 1994 to 1997 were used to determine DIN/DIP elemental ratios for each month that data were collected. The results, depicted in Figure 8, show high DIN: DIP ratios during the spring and early summer and lower ratios during the late summer and fall. The DIN: DIP ratios during the spring and early summer were often well above the Redfield ratio of 16:1, indicative of the potential for phosphorus limitation. The lower DIN: DIP ratios during the late summer and fall are closer to the Redfield ratio, and this would be consistent with either phosphorus or nitrogen limitation, or co-limitation by both nutrients. More sampling is needed across the hypoxic area of the northern Gulf to better characterize the spatial and temporal variations in nutrient concentrations.

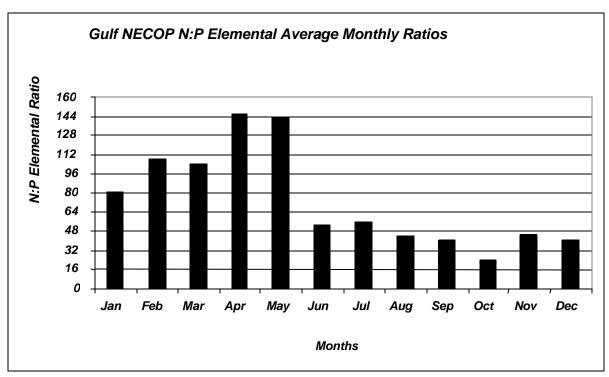


Figure 9. Average monthly DIN/DIP Elemental Ratios from Transect C Sampling, 1994, 1995 and 1997.

Highest chlorophyll concentrations along Transect C in the eastern portion of the Hypoxic Zone were observed during the spring and early summer of 1997(Figure 9). This would be expected to coincide with the period of highest productivity. Consistent with this view, in an analysis of monthly composite chlorophyll data for Transect C stations C6, C6A, and C6B for the years 1985-1997, Rabalais and Turner (2001) reported that chlorophyll concentrations were generally highest during April and May and lower in the late summer months. This would suggest that, at these stations along Transect C, a large portion of the annual primary productivity occurs during the spring and early summer. Rabalais and Turner (2001) also refer to several studies showing relatively high abundance of copepod zooplankton, and the production of copepod fecal pellets during the spring and early summer.

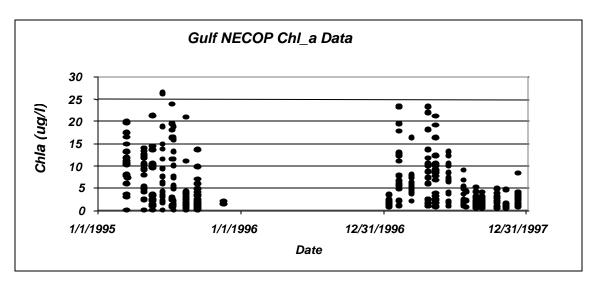


Figure 10. Chl_a Concentrations along Transect C, 1995 and 1997.

Rabalais et. al., 1999 (Section 6.5, pages 75-77) concluded that the phytoplankton, copepod zooplankton, and copepod fecal pellets were produced in quantity during the spring and early summer growing season; that this productivity was the likely source of organic matter that sinks to the lower water strata and decays; and that the organic matter produced during the spring and early summer consumes dissolved oxygen and is a major factor contributing to hypoxia.

The available evidence indicates a potential for phosphorus limitation in the lower salinity waters of the northern Gulf of Mexico during the spring and early summer – an area immediately impacted by the Mississippi River discharge and nutrient loading. It is interesting to note that the Redfield ratios in the Hypoxic Zone, Transect C are 2-3 times greater than the Redfield ratios calculated for the Mississippi River. This can be explained if significant algal production occurs in the Mississippi River plume as it migrates to Transect C. Assuming the nutrients in the Mississippi River plume are consumed in Redfield ratio proportions, 16:1, the remaining nutrient ratio increases as the phosphorus is depleted relative to the excess nitrogen depletion. This occurs only when phosphorus is the limiting nutrient. This primary production zone of biomass, from the River mouth to Transect C likely accounts for a substantial portion of the primary productivity causing hypoxia. No other substantial algal production zone was identified in the CENR Report, although speculation that such sites exist was stated. Nitrogen limitation appears to be confined to the higher salinity areas, especially during the late summer and fall. The higher salinity areas usually have low nutrient concentrations due to nutrient depletion by phytoplankton and dilution with low nutrient offshore waters. These high salinity areas normally exhibit low primary productivity.

The pattern of phosphorus limitation during the spring and early summer and nitrogen limitation during the late summer and fall is not unique to the Mississippi and Atchafalaya river system. Fisher et al. (1992) described such a pattern for the Chesapeake Bay, based on comprehensive water quality sampling and nutrient loading studies. Fisher et al. (1999) also conducted comprehensive and very sophisticated nutrient addition studies for the Chesapeake Bay. These studies confirmed extensive phosphorus limitation in the Chesapeake Bay during the spring and early summer and nitrogen limitation during the late summer and fall. Accordingly, decreasing phosphorus and nitrogen loading to the Chesapeake Bay, to control excess phytoplankton production during the spring and early summer, is an integral part of the control strategy for the Bay.

SUMMARY

The available Gulf hypoxia data and related scientific literature provide support for a hypothesis that the Northern Gulf waters are subjected to nitrogen and phosphorus loads significantly above historic background levels, and there may be benefit to reducing both nutrients in order to mitigate the Hypoxic Zone. While the *Action Plan* calls for appropriate voluntary action to address nitrogen loading, this paper provides an analysis to support a reevaluation of the potential role of phosphorus load reduction as well. An outcome of the reevaluation, if supported by peer review, would be the development of a balanced approach to reducing <u>both</u> nutrients to achieve the first and second goals of the *Action Planto mitigate the extent of the Gulf Hypoxic Zone and* – to restore water quality throughout the Mississippi River Basin.

REFERENCES CITED

Ammerman, James W. 1992. Seasonal Variation in Phosphate Turnover in the Mississippi River Plume and the Inner Gulf Shelf: Rapid Summer Turnover. In Proceedings, Nutrient Enhanced Coastal Ocean Productivity

Workshop. Publication No. TAMU-SG-92-109. Texas Sea Grant College Program. Texas A&M University, College Station Texas. 69-75.

Capone, D. G. (2001). Marine nitrogen fixation: what's the fuss? Current Opinion in Microbiology, vol. 4: 341-348.

Chen, Xiaogang. 2000. Distributions and Variations of Phytoplankton Photosynthesis and Primary Production on the Louisiana –Texas Continental Shelf. PH. D. Dissertation University of Southern Mississippi.

Correll, David L. 1998. The Role of Phosphorus in the Eutrophication of Receiving Waters: A Review. Journal of Environmental Quality. 27:261-266.

DeMaster, David J., and Robert H. Pope. 1996. Nutrient Dynamics in Amazon Shelf Waters: Results from AMASSEDS. Continental Shelf Research. Vol. 16, No. 3, pp. 263-289.

Dortch Q., and T. E. Whitledge (1992) Does Nitrogen or Silicon Limit Phytoplankton Production in the Mississippi River Plume and Nearby Regions? Continental Shelf Research 12:1293-1309.

Fisher, T. R., Peele, E. R., and Harding, L. W. (1992) Nutrient Limitation of Phytoplankton in Chesapeake Bay. Marine Ecology. Prog. Ser. 82:51-63.

Fisher, T. R., et al. 1999. Spatial and Temporal Variation of Resource Limitation in Chesapeake Bay. Marine Biology. 133:763-778.

Goolsby, D. et al. (1999) - Flux and Sources of Nutrients in the Mississippi-Atchafalaya River Basin. CENR Report No. 3.

Hendee, James C. 1994. Data Management for the Nutrient Enhanced Coastal Ocean Productivity Program. Estuaries. Volume 17. No. 4. pp. 900-903.

Hoyer, Mark V., Thomas K. Frazer, Sky K. Notestein, and Daniel E. Canfield, Jr. 2002. Nutrient, Chlorophyll, and Water Clarity Relationships in Florida's Nearshore Coastal Waters with Comparisons to Freshwater lakes. Canada Journal Fisheries and Aquatic Science. 59:1024-1031.

Justic, Dubravko, Nancy N. Rabalais, and R. Eugene Turner, 1995. Stoichiometric Nutrient Balance and Origin of Coastal Eutrophication. Marine Pollution Bulletin, Vol. 30, No.1, pp. 41-45.

Justic, Dubravko, Nancy N. Rabalais, and R. Eugene Turner. 2002. Modeling the Impacts of Decadal Changes in Riverine Nutrient Fluxes on Coastal Eutrophication near the Mississippi River Delta. Ecological Modeling. Volume 152, Issue 1, pp. 33-46.

Justic, Dubravko, Nancy N. Rabalais, and R. Eugene Turner. 2003. Simulated Responses of the Gulf of Mexico Hypoxia to Variations in Climate and Anthropogenic Nutrient Loading. Journal of Marine Systems. 42:115-126.

Kustka, A., E. Carpenter and S. A. Sanudo-Wilhelmy (2002). Iron and marine nitrogen fixation: progress and future directions. Research in Microbiology, vol. 153: 255-262.

Lohrenz, S. E., G. L. Fahnensteil, D. G. Redalje, G. A. Lang, M...J. Dagg, T..E. Whitledge, and Q. Dortch (1999) The Interplay of Nutrients, Irradiance, and Mixing as Factors Regulating Primary Production in Coastal Waters Impacted by the Mississippi River Plume. Continental Shelf Research. 19:1113-1114.

Moore, J.K., S.C. Doney, D.M. Glover and I.Y. Fung (2001). Iron cycling and nutrient-limitation patterns in surface waters of the World Ocean. Deep-Sea Research, Part II: Topical Studies in Oceanography, vol. 49: 463-507.

Rabalais, Nancy N., R. Eugene Turner, Dubravko Justic, Quay Dortch, and William J. Wiseman, Jr. 1999. Characterization of Hypoxia: Topic 1 Report for the Integrated Assessment on Hypoxia in the Gulf of Mexico. NOAA Coastal Ocean Program Decision Analysis Series No.15. NOAA Coastal Ocean Program, Silver Spring, MD. 167 pp.

Rabalais, Nancy N. and R. Eugene Turner (2001) Coastal Hypoxia: Consequences for Living Resources and Ecosystems. Coastal and Estuarine Studies, Pages 1-36. American Geophysical Union.

Rabalais, Nancy N., R. Eugene Turner, Quay Dortch, Dubravko Justice, Victor J. Bierman and William J. Wiseman. 2002. Nutrient-Enhanced Productivity in the Northern Gulf of Mexico: Past, Present, and Future. Hydrobiologica. 475/476: 39-63.

Redfield, A. C. 1958. The Biological Control of Chemical Factors in the Environment. American Scientist. 46:1-221.

Riley, Gordon A. 1937. The Significance of the Mississippi River Drainage for Biological Conditions in the Northern Gulf of Mexico. Journal of Marine Research.1 (1): 60-74.

Smith, S.M., Hitchcock, G. L. 1994. Nutrient Enrichment and Phytoplankton Growth in the Surface Waters of the Louisiana Bight. Estuaries. 17, 740-753.

Walker, William W. .1999. Simplified Procedures for Eutrophication Assessment and Prediction: User Manual

Station	Station Name	PCode	Units	# Obs	Mean	Min	Max	Firs Dat
USGS07374525	MISSISSIPPI R @ BELLE CHASSE, LA	FLOWCFS	cfs	155	547,322.58	0.08	1,070,000.00	09/(
USGS07374525	MISSISSIPPI R @ BELLE CHASSE, LA	NH3	mg/L	140	0.1	0	2.2	09/(
USGS07374525	MISSISSIPPI R @ BELLE CHASSE, LA	NO2NO3	mg/L	140	1.59	0.03	14.2	09/(
USGS07374525	MISSISSIPPI R @ BELLE CHASSE, LA	NOXNH4	mg/L	139	1.45	0.11	2.84	10/(
USGS07374525	MISSISSIPPI R @ BELLE CHASSE, LA	PORTHO	mg/L	111	0.09	0.01	0.3	10/(